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# Tricontinuous Cubic Structures in $ABC/A/C$ Copolymer and Homopolymer Blends

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Using the Monte Carlo lattice-simulation technique, we present numerical evidence of the formation of gyroid and nongyroid tricontinuous cubic phases in high polymeric systems of  $ABC/A/C$  triblock copolymer and homopolymer blends. By increasing the volume fraction of homopolymer, a remarkable phase sequence  $G$  (gyroid)  $\rightarrow D$  (diamond)  $\rightarrow P$  (primitive) is observed, which is common to certain surfactant systems. Our results indicate that the  $ABC$  triblock copolymer system with blending homopolymers may be a zoo of cubic phases, suitable for comparative studies of these phases.

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Biological amphiphilies (lipids) or synthetic surfactants in aqueous solutions self-assemble to bilayers centered on the multiply connected surface dividing the space into two interpenetrating and nonintersecting “bicontinuous” subspaces [1]. At high concentration of lipids or surfactants, these bilayers can organize cubic phases based on mathematically well-characterized surfaces, namely, multiply periodic minimal surfaces; e.g., Schoen-Luzatti gyroid ( $G$ ), Schwarz diamond ( $D$ ), Schwarz primitive ( $P$ ), and Neovius surface [ $C(P)$ ] [2]. Moreover, it is known that these surfaces abound in biological cells such as the endoplasmic reticulum, the mitochondrion, and the nucleus of certain cells [3]. For high polymeric block copolymer systems [4], bicontinuous cubic phases had attracted much attention as well [5–7]. In plastic technologies, high polymeric bicontinuous systems are thought to be promising candidates of future technologies such as photonic crystals [8], although it is believed [4] that only the  $G$  phase has been established in most block copolymer systems [9,10]. Is there any systematic route to find nongyroid cubic phases in high polymeric systems?

In this Letter, with recourse to Monte Carlo (MC) technique [11] using the diagonal bond method [12,13], we conjecture nongyroid cubic tricontinuous mesophases in  $ABC$  (linear) triblock copolymer systems with blending homopolymer. Here we employ  $AC$  symmetric  $ABC$  triblock copolymers as ingredients of surfaces separating phases rich in  $A$  and  $C$  homopolymers. Our tricontinuous spaces consist of one strut composed of  $A$  polymers and the other strut composed of  $C$  polymers separated by a  $B$ -polymer region. Additional homopolymers act as solutions in surfactant or lipid systems. Recently, Fredrickson and Bates [14] have suggested “polymeric microemulsions” by using the same  $ABC$  triblock copolymers as surfactants; in their study, the concentration of homopolymers is much greater than that of our investigation. Our focus is to seek for well-organized structures.

Recently, there arose a number of numerical studies in search of gyroid or gyroidlike structures in  $AB$  block copolymers [2,15–17]. Nevertheless, we chose  $ABC$  tri-

block copolymer systems because of two reasons. First, the multicontinuous region is wider than that of diblock systems [6,10]. Second, in practice, the  $ABC$  system is much better than  $AB$  systems. In the case of  $AB$  systems, two struts tend to intersect by forming the complex of struts or perforated lamellae, because the two struts are composed of the same component. On the contrary, in the case of the  $ABC$  system, two struts consist of  $A$  and  $C$ ; accordingly, they can repel each other by energetics. Correspondingly, different kinetic pathways may be expected [17].

We point out that, in any simulation methods applied to block copolymer systems, fine-tuning box sizes to periods of ordered structures is crucially important [18]. We search and compare structures with changing simulation box size in order to select a stable phase. As a result, we have found the formation of the unit cell of different cubic phases with changing system size  $L$ . We determine the most probable structure by the formation of twice-periodic structure; first, because the possibility of the formation of twice-periodic false states competing with the true state is supposed to be quite low, and, second, because enforcement by the boundary conditions does not work as in the case of one period as we shall later see.

Our simulation method is a simple but dramatically effective extension of a Verdier-Stockmayer-type coarse-grained bead-and-bond lattice polymer MC simulation method. A model  $ABC$  triblock copolymer and homopolymer consist of  $N = 22$ ;  $[N_A, N_B, N_C] = [5, 12, 5]$ , and  $N_{hA} = 5$  and  $N_{hC} = 5$  beads. The bond length is 1,  $\sqrt{2}$ , or  $\sqrt{3}$  in the unit of lattice spacing. Equal number densities of two kinds of homopolymers are prepared. The number of polymers in a system is determined such that the occupation ratio of beads in the lattice points is 0.75. Vacancies act as nonselective solvents. To represent energetics that drives the system to microphase separation, unit interaction energies are imposed only between pairs of different components within the body diagonal distance  $\sqrt{3}$ : We consider the Hamiltonian as  $H = \sum \epsilon_{ij}$ , where  $\epsilon_{ij} = 1$  when  $i \neq j$ , and  $i$  and  $j$  stand for  $A$ ,  $B$ , and  $C$ . The system is usually prepared at first as totally

randomized at the infinite temperature, and then quenched at  $\beta = 1/k_B T = 0.15$  ( $\chi N = 59.4$ ) or  $\beta = 0.2$  ( $\chi N = 79.2$ ) to wait ordering, where  $k_B$  is the Boltzmann constant,  $T$  is absolute temperature, and  $\chi = 18\beta\epsilon$  is the interaction parameter.

We have performed several compositions of copolymers and homopolymers. In this paper, we describe the typical three systems: (I)  $\phi_{co} = 1.0$ ,  $\phi_{hA} = \phi_{hC} = 0$ ,  $\phi_B = 0.545$ , ( $\chi N = 59.4$ ); (II)  $\phi_{co} = 0.8$ ,  $\phi_{hA} = \phi_{hC} = 0.1$ ,  $\phi_B = 0.436$ , ( $\chi N = 59.4$ ); (III)  $\phi_{co} = 0.667$ ,  $\phi_{hA} = \phi_{hC} = 0.167$ ,  $\phi_B = 0.3636$ , ( $\chi N = 79.2$ ), corresponding to single  $G$  (space group  $I4_132$ ), single  $D$  ( $Fd\bar{3}m$ ), and single  $P$  ( $Pm\bar{3}m$ ) phases [19], where  $\phi_{co}$ ,  $\phi_{hA}$ ,  $\phi_{hC}$ , and  $\phi_B$  are the volume fractions of copolymer, A and C homopolymer, and B component.

(I) The pure system made up of only ABC block copolymers is known to form the  $G$  phase [10]. In our numerical experiments, a single period of the  $G$  structure has been obtained for sizes from  $L = 23$  to  $L = 27$ , and a single unit cell of the  $D$  structure has been obtained from  $L = 32$  to  $L = 35$  as well. There is no  $P$  phase down to  $L = 16$ . However, twice-periodic formation has been found only for the  $G$  phase with  $L = 52$  by a run of several  $10^5$  Monte Carlo steps (MCS); hence, we safely conclude that the  $D$  phase is ruled out. With respect to the composition change in the ABC copolymer, in the system of  $[N_A, N_B, N_C] = [4, 14, 4]$ , the  $G$  phase has been obtained for  $L = 50, 52$ , and in the case of  $[3, 16, 3]$ , the  $G$  phase has been found for  $L = 48$ ; hence, the range  $\phi_B = 0.545\text{--}0.727$  corresponds to the  $G$  phase, which is consistent with experiments. In Fig. 1, an example of the growth of the  $G$  phase for a  $[N_A, N_B, N_C] = [4, 14, 4]$  system is shown. The number of copolymers in the cube  $L^3$  with  $L = 52$  is  $n_{ABC} = 4793$ .

(II) This system turned out to form the  $D$  phase. One period of the  $P$  structure has been obtained for sizes from  $L = 20$  to  $L = 27$ , that of  $G$  has been obtained from  $L = 29$  to  $L = 34$ , and that of  $D$  has been obtained from  $L = 41$  to  $L = 43$ . In other regions, we have obtained defective cubic phases or ill-ordered ones. It is important that two periods of  $P$  and  $G$  structures have not been obtained; however, we have succeeded in forming defect-free two periods of the unit cell of the  $D$  phase for  $L = 82$  by a run of  $8 \times 10^6$  [20] as shown in Fig. 2. Figure 3 shows energy per bead and mean square end-to-end distance as functions of MCS. The number of polymers in the cube  $L^3$  with  $L = 82$  is  $n_{ABC} = 15037$  and  $n_A + n_C = 16542$ . Another evidence is that we have obtained a defective but almost perfect twice-periodic  $D$  structure for  $L = 86$  by quenching at  $\beta = 0.2$ .

(III) This system turned out to form the  $P$  phase. One period of the  $P$  structure has been obtained for sizes from  $L = 23$  to  $L = 37$ , and the  $G$  has been obtained from  $L = 38$  to  $L = 41$ . We did not find perfect  $D$  structures, but defective  $D$  structures were formed for  $L = 54$  and  $L = 57$ . Furthermore, we have obtained two periods of

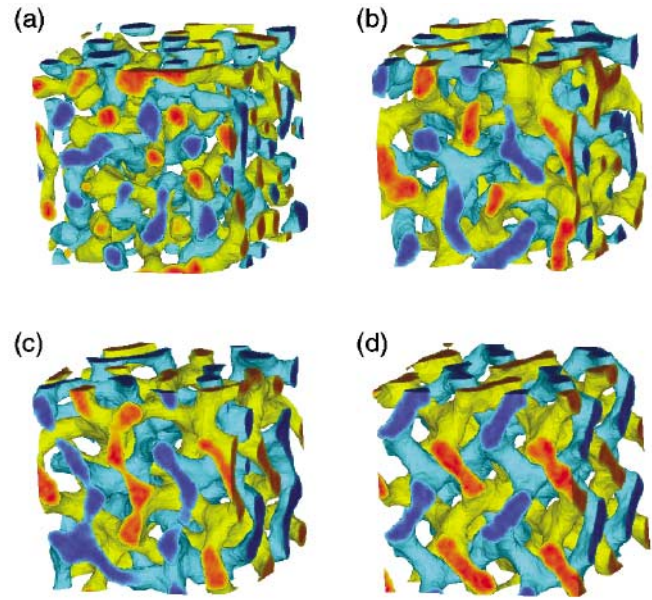


FIG. 1 (color). Growth of a gyroid ( $G$ ) phase: Quenching at  $\beta = 0.15$  for a pure ABC copolymer melt in a cube ( $L^3$  with  $L = 52$ ). (a)  $10^4$ , (b)  $2 \times 10^5$ , (c)  $4 \times 10^5$ , and (d)  $6 \times 10^5$  Monte Carlo steps. In each picture, the Monte Carlo average over 1000 steps was taken. In the last picture, a two-periodic  $G$  phase is depicted by twin (A: blue; C: yellow) three-pronged interpenetrating networks.

the  $P$  structure for  $L = 69$  by quenching at  $\beta = 0.2$ , then  $\beta = 0.3$ , and finally  $\beta = 0.5$ .

Some remarks about (III) are the following. (i) Starting with the condition for homopolymers in one side of the simulation box, and for copolymers in the other side of the box, we have obtained a twice-periodic  $P$  structure in a box with  $L = 66$  at  $\beta = 0.2$  (Fig. 4). The number of polymers in the cube  $L^3$  with  $L = 66$  is  $n_{ABC} = 6534$  and  $n_A + n_C = 14375$ . Up to  $L = 100$ , there is no indication of any macrophase separation nor phase coexistence. (ii) Upon lowering temperature, interfaces tend to

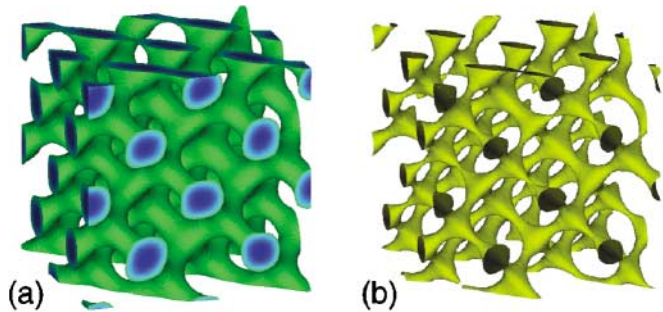


FIG. 2 (color). Diamond ( $D$ ) phase: Simulation result ( $L^3$  with  $L = 82$ ) of a blend ABC/A/C system with volume ratio 8:1:1. The MC average over 20000 steps was taken at a low temperature. (a) A monomers of ABC copolymers and A homopolymers forming a single diamond network. (b) A homopolymers. Homopolymers tend to gather at four-pronged tetrapodlike nodes. The figures correspond to twice the unit cell.



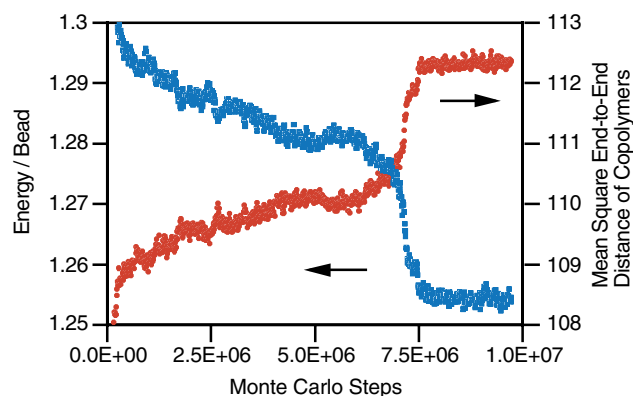


FIG. 3 (color). Energy per bead and mean square end-to-end distance of *ABC* copolymers vs Monte Carlo steps are shown. A rapid drop in energy and a rise in mean square end-to-end distance correspond to the final formation of a twice-periodic *D* structure.

become more flat leading to increasing the lattice constant. Since the volume ratio of three components (*A*, *B*, *C*) is almost the same, the competition to form lamellae may be important. (iii) We have been able to form twice-periodic *P* structures for the system with longer chains:  $[N_A, N_B, N_C, N_{hA}, N_{hC}] = [7, 16, 7, 7, 7]$ .

Although the evaluation of free energy is required, we deduce that the behavior of homopolymers tending to concentrate in nodes of struts is an important factor to drive the system to form the nongyroid cubic phases, whose term does not exist in surfactant systems. As depicted in Figs. 2(b) and 4, most of the homopolymer fills the nodes of the structures connected by narrow branches. Obviously, Fig. 4 illuminates why the *P* structure has not been obtained in pure triblock copolymer systems, since too much stretching of *A* and *C* parts is inevitable. Homopolymers entropically tend to concentrate in nodes not only because they relax the stretch of *A* and *C* parts, but also because the confinement of homopolymer is weaker than in narrow branches [21]; the *G* is three-pronged, the *D* is four-pronged, and the *P* is six-pronged; the greater the number of prongs, the larger the excess volume of nodes [22].

Ström and Anderson, for didodecyldimethylammonium bromide in water and styrene, and Landh, for pine oil monoglycerides in water and poloxamer, have found marvelous lyotropic phase behavior, a phase sequence of bicontinuous cubic phases in surfactant solutions with increasing water [23]. The common sequence is  $G \rightarrow D \rightarrow P \rightarrow C(P)$ . This progression has been accounted as a “universal” feature of the geometry of minimal surfaces, i.e., system independent space-filling and space-dividing requirements of cubic bicontinuous phases [23,24]. Hence, one may expect that it can be applied not only to surfactant systems but also to block copolymer systems. In this context, it should be noted that Matsen [25] has already predicted a  $G \rightarrow D$  phase tran-

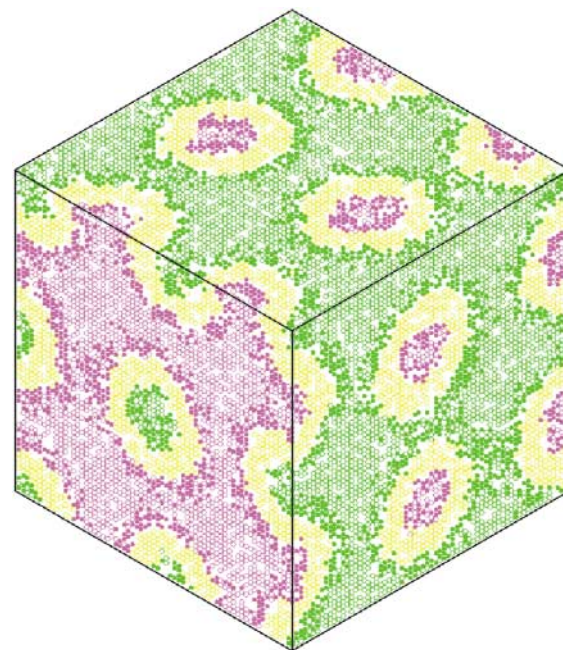


FIG. 4 (color). Primitive (*P*) phase: A snapshot at  $\beta = 0.2$  in a cube ( $L^3$  with  $L = 66$ ) for a blend *ABC/A/C* system with volume ratio 4:1:1. Monomers of *ABC* copolymers (*A*: pink solid circle; *B*: yellow circle; *C*: green solid circle) and monomers of homopolymers (*A*: pink open circle; *C*: green open circle) are displayed. Notice that most homopolymers stay inside nodes, rather than inside six-pronged branches.

sition with the addition of minority component homopolymer into *AB* block copolymer melts, and shown the accumulation of homopolymer at nodes relaxing interfaces to constant mean curvature surfaces, which are favored by the interfacial tension [26].

Generally, the phase behavior of surfactant systems is strongly affected by their chemical details: Even in the blessed case of Ström and Anderson, the choice of styrene was crucially important to see the phase progression. Furthermore, fluctuations are apt to obscure ordering in surfactants. In contrast, these effects are weaker in high polymeric systems; therefore, we presume that block copolymer/homopolymer blends may provide better cases as generic self-assembling models. Finally, we note that the lattice MC method is of greatest utility to investigate such fundamental phase behavior.

*Note added.*—Recently, Wiesner *et al.* [27] have found a *P* phase in mixtures of copolymer and homopolymer (PI-*b*-PEO/ceramic precursor). This supports the idea that blending homopolymer could be a key to form nongyroid cubic phases as shown in our simulation.

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